Preparation of Lactones *via* Tricarbonyliron–Lactone Complexes

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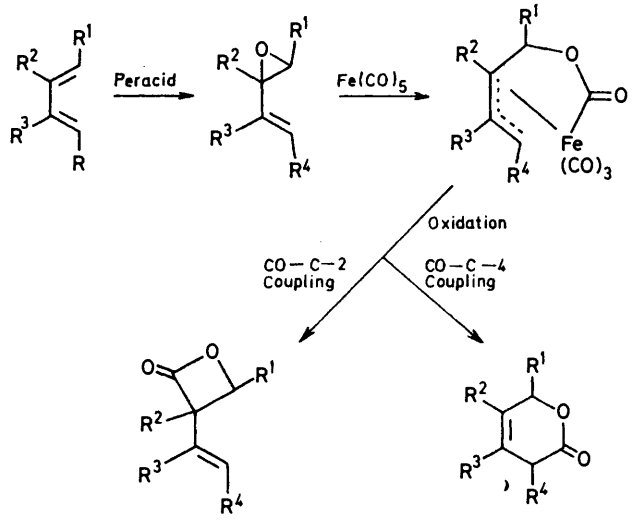
A number of tricarbonyliron–lactone complexes have been prepared from vinyl oxirans by treatment with pentacarbonyliron. In certain cases two η^3-allyl complexes were isolated from a single vinyl oxiran. Oxidation of the complexes by cerium(IV) ammonium nitrate in acetonitrile leads predominantly to β-lactones. The stereochemical integrity of the initial complexes is reflected in the formation of the oxidation products. Reduction of these products with lithium aluminium hydride gave the expected diols.

THE use of tricarbonyliron complexes is now an established strategy in the synthetic chemists' repertoire.[1] While synthetic equivalents for the addition of carbon dioxide to dienes are known, they often require high



SCHEME 1

temperatures or pressures and are not necessarily regiospecific.[2] We argued that dienes, *via* their monoregiospecific epoxide derivatives, could be converted into tricarbonyliron–lactone complexes, which on oxidation could lead to either δ- or β-lactones depending on which carbon atoms became coupled (Scheme 1).

RESULTS AND DISCUSSION

A number of tricarbonyliron lactone complexes have been prepared previously;[3] however, their use in synthesis had not been fully explored. The tricarbonyliron–lactone complexes (1)—(12) were prepared by treatment of the corresponding vinyloxiran with $Fe(CO)_5$. The vinyloxirans (13)—(21) were readily available by peracid oxidation of the dienes (22)—(28) or in certain cases [(17) and (20)] by reaction of the enals (29) and (30) with dimethylsulphonium methyl ylide, $(CH_3)_2\overset{+}{S}-\bar{C}H_2$.[4]

The dienes (22) and (28) were obtained commercially while the others were synthesised by standard routes. For example, both (23) and (24) were prepared by dehydration of the corresponding alcohols formed from vinylmagnesium bromide addition to cyclopentanone and cholestanone, respectively. The diene (25) was obtained by pyrolysis of the diacetate (31) at 520 °C[5] and the diene (27) was derived from the alcohol (32) by reductive rearrangement with lithium aluminium hydride.[6]

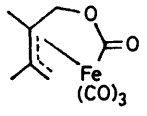
Finally, (26) was prepared as a 50 : 50 mixture of *cis*- and *trans*-isomers from palladium(II)-catalysed elimination[7] of the acetate (33). Epoxidation of the dienes with *m*-chloroperbenzoic or peracetic acid proceeded smoothly (see Experimental section).

The formation of the tricarbonyliron–lactone complexes from the vinyloxirans, however, requires further comment.

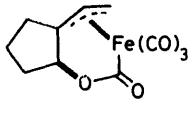
In order that optimum yields of complexes could be obtained, we found that the use of Chance OX-1 or sodium bromide filters[8] were desirable under the photochemical conditions.

In the formation of the complexes (1), (6), (7), and (10)—(12) the reaction proceeded normally to yield single isomers. However, the vinyloxirans, (14), (15), and (18) with pentacarbonyliron, $Fe(CO)_5$, lead to the isolation of two isomeric complexes from each of the reactions.

Thus, (14) with $Fe(CO)_5$ gave the *syn*-ferralactone (2) and the *anti*-ferralactone (3) in the ratio 6 : 1 in 79% overall yield. The *syn*- and *anti*-notations are used to represent the position of the iron moiety with respect to the bridge oxygen atom.



(1)



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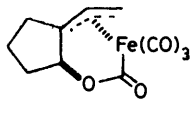
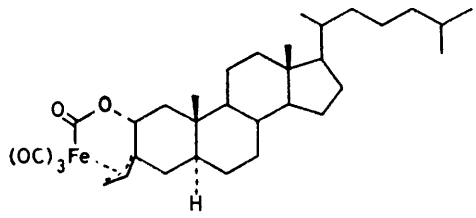


(3)

As spectroscopic analysis failed to absolutely confirm these structures, we resorted to *X*-ray crystallographic methods. These data[9] also show that the carbon atom at the terminus of the η^3-allyl system is some 0.24 Å out-

of-plane relative to the neighbouring carbon atoms and thus indicates its high sp^3 character.

Of particular interest is that these complexes, (2) and (3), behave differently towards oxidation (see below). Isolation of isomeric complexes from vinyloxirans had not been noticed previously under photochemical conditions.[3d] In a similar fashion, the vinyloxiran (15) lead to two lactone complexes (4) and (5) being isolated in a 1 : 1 *syn* : *anti* ratio. While the spectroscopic data are fully in accord with their structures, final structural evidence was provided by their individual characteristics on oxidation.



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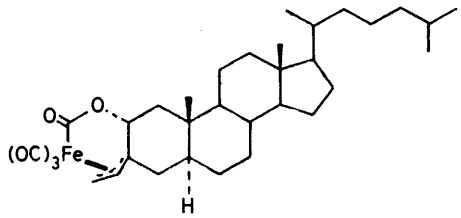
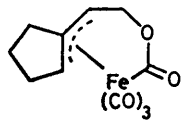


(5)

Reaction of (1) with Ce^{IV} in aqueous ethanol gave the δ-lactone (34) in 38% yield as the only isolable product. Oxidation in acetonitrile, however, gave the δ-lactone (34) (16%) as a minor product, the major one being the β-lactone (35) (42%). The i.r. spectrum of (35) shows the characteristic strained-ring lactone-carbonyl group at 1 825 cm^{-1}. The ^1H n.m.r. has absorptions for the methyl groups at δ 1.83 and 1.6, a broad singlet at 4.96 (2 H) for the vinylic protons and an AB quartet at 4.05 and 4.28 (J 5.5 Hz) corresponding to the non-equivalent methylene protons. The δ-lactone (34) was compared spectroscopically with an authentic sample.[10]



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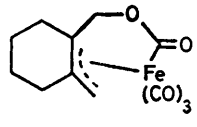

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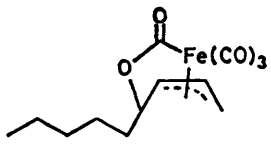

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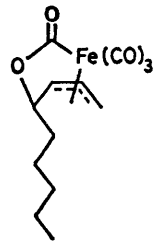

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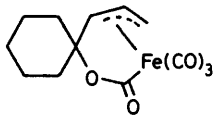
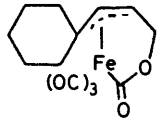


(10)



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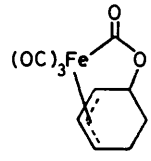


(12)

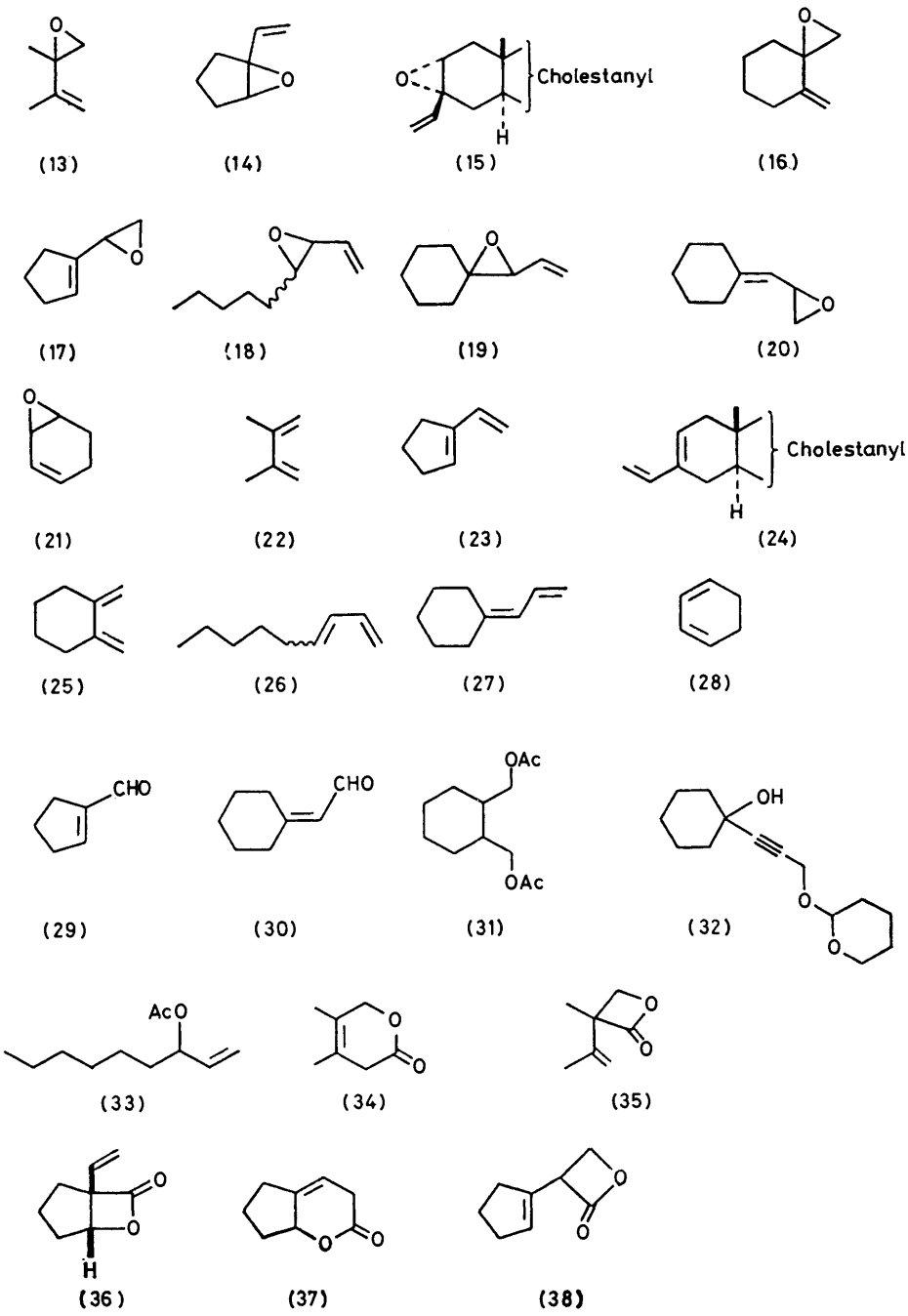
Lastly, treatment of (18) with $Fe(CO)_5$ provides two complexes, (8) and (9). The structural assignment of these species follows from a comparison with other complexes reported in the literature.[3d]

With the tricarbonyliron–lactone complexes to hand, their oxidation with cerium(IV) ammonium nitrate was investigated. Other oxidants studied proved to be less satisfactory.

Oxidation of the *syn*-complex (2) with cerium(IV) ammonium nitrate in acetonitrile also gave a mixture of β- and δ-lactones; compounds (36) and (37) respectively. These lactones were formed in good combined yield (80%) with the β-lactone predominating. The *anti*-isomer (3), however, afforded (37) as the only product on oxidation in 75% yield. A corresponding β-lactone from this oxidation would have been *trans*-fused to the

cyclopentane ring and, therefore, is precluded by ring strain.

This result indicates that the stereochemical integrity of the initial complex dominates the formation of the spectrum, the lactone (39) displays an absorption in the ^{1}H n.m.r. at δ 4.65 as a one-proton doublet of doublets (J 1.5 and 8 Hz) corresponding to the C-2 proton jointly coupled to the C-1 protons.



(13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38)

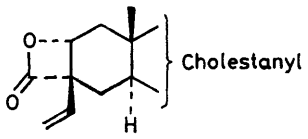
products. This observation was also confirmed in later experiments.

The *syn*-cholestanyl complex (4) for example gave both the β-lactone (39) ($\nu_{max.}$ 1 830 cm^{-1}) and the δ-lactone (40) ($\nu_{max.}$ 1 730 cm^{-1}) whilst the *anti*-isomer (5) afforded (40) exclusively. Apart from the characteristic i.r.

Oxidation of (6), which can be considered as the regioisomer of (2) and (3), gave remarkably the β-lactone (38) in essentially quantitative yield after low temperature (0 °C) column chromatography. On the other hand, the tricarbonyliron complex (7) gave the δ-lactone (42) (55%) on oxidation. The β-lactone (41) was also

produced in this reaction but in only 15% yield. The ^{1}H n.m.r. of (41) shows important absorptions at δ 4.85 and 4.6 (1 H, broad singlets) and an AB quartet at 3.65, 3.35 (*J* 5.5 Hz).

Oxidation of (8) and (9) are more interesting in that (8) leads exclusively to the *trans*-β-lactone (44) (68%), and (9) gives specifically the *cis*-β-lactone (45) (64%). The ^{1}H n.m.r. spectra of these lactones show a coupling of



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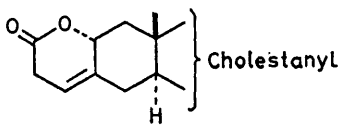

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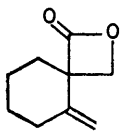

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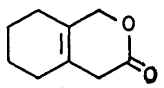
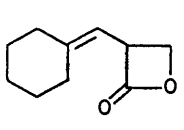


(42)

4 Hz for the *trans*-protons of the β-lactone ring in (44) whereas (45) shows the *cis*-protons coupled by 7 Hz, which are typical values for other β-lactone ring systems.[11]

The remaining examples that we studied, (10)—(12) all gave β-lactones, (46), (43), and (47), respectively on treatment with Ce^{IV} in the appropriate solvent. These results illustrate further the preferential formation of the smaller-ring lactone.

The β-lactones containing a vinyl substituent α to the carbonyl group presented here form a relatively new class of β-lactone, as very few other examples exist in the literature.[12] Owing to the tendency of many of the



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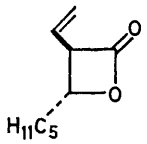

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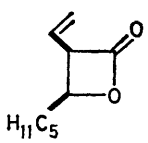

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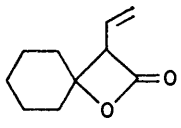

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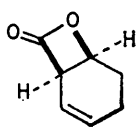
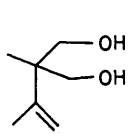


(47)

lactones prepared above to be unstable they were additionally characterised by reduction to the corresponding diols (48)—(56) using lithium aluminium hydride.

The mechanism for the production of the lactones from tricarbonyliron complexes must take into account the preferential formation of β- *versus* δ-lactones, and also the observed retention of the initial stereochemical features. The *X*-ray data of the complexes clearly show that high sp^3 character already exists at the terminal carbon, and often more substituted carbon, of the



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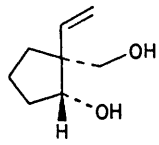

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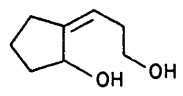

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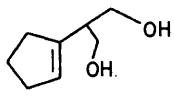

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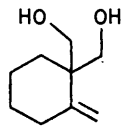

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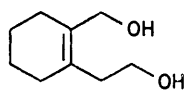

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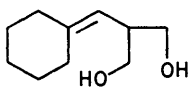

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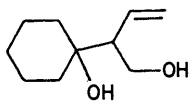

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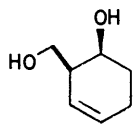
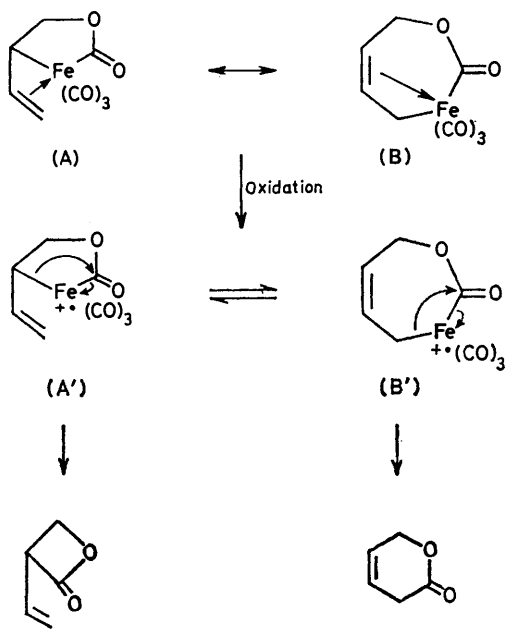


(56)

η^3-allyl unit. The canonical forms (A) and (B) (Scheme 2) therefore contribute to the overall resonance hybrid structure. Oxidation of (A) by (B) could lead to an equilibrating mixture of intermediate radical cations (A′) or (B′) which on concerted fragmentation would



(A) (B) (A′) (B′)

SCHEME 2

give the β- and δ-lactones. More rapid decomposition of (A′) would lead to the preferentially formed β-lactones.

Should oxidative decomposition take place *via* possible allylic cation intermediates we would have anticipated that either solvent trapped products, or structurally isomerised products, would have been obtained.

The above preferential formation of β-lactones from tricarbonyliron–lactone complexes by oxidation with Ce^{IV} complements the recent observation by Aumann [13] that under high carbon monoxide pressures (200—300 atm) and temperature (70 °C) similar complexes can be converted to δ-lactones.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^1H N.m.r. spectra were obtained for solutions in $CDCl_3$ ($SiMe_4$ as internal standard). Petroleum refers to the fraction of b.p. 40—60 °C. Solutions were dried over sodium sulphate and solvents by literature methods. Chromatography was performed on Merck-Kieselgel 60 (0.04—0.063 mm) and B.D.H. Florisil (200—300 U.S. mesh).

General Procedure for Vinyloxiran Preparation. Method A.—*m*-Chloroperbenzoic acid (*m*-CPBA) was added portionwise to a stirred slurry of the diene and sodium carbonate in methylene chloride at 0 °C. After all the peracid had been consumed (as shown by starch–iodide paper) the mixture was filtered and the precipitate washed with methylene chloride. Removal of the solvent from the filtrate gave an oil which was distilled under reduced pressure to afford the pure vinyloxiran.

Method B.—The diene was added to a mixture of anhydrous sodium carbonate in methylene chloride cooled to 0 °C. To this suspension was added peracetic acid containing a catalytic amount of sodium acetate over a period of 1 h. After completion, the mixture was allowed to warm to room temperature, filtered and worked up as above.

2,3-Dimethyl-3,4-epoxybut-1-ene (13).—2,3-Dimethylbuta-1,3-diene (22) (1.4 g, 17 mmol) was oxidised with *m*-CPBA (3.25 g, 17 mmol 85%) in CH_2Cl_2 (200 ml) to afford the vinyloxiran (13) (1.0 g, 60%); δ 5.1 (1 H, br s), 5.0—4.91 (1 H, m), 2.72 (2 H, s), 1.74 (3 H, s), and 1.45 (3 H, s).

1,2-Epoxy-1-vinylcyclopentane (14).—1-Vinylcyclopent-1-ene (23) (3.2 g, 34 mmol) on oxidation with *m*-CPBA (5.87 g, 34 mmol) in CH_2Cl_2 (240 ml) containing saturated sodium carbonate (60 ml) afforded the *vinyloxiran* (14) (2.1 g, 59%), b.p. 50 °C at 10 mmHg; δ 5.86 (1 H, dd, *J* 10 and 17 Hz), 5.48—5.08 (2 H, m), 3.35 (1 H, br s) and 2.35—1.15 (6 H, m) (Found: M^+, 110.072 9. $C_7H_{10}O$ requires *M*, 110.073 2).

2α,3α-Epoxy-3β-vinyl-5α-cholestane (15).—3-Vinylcholest-2-ene (24) (5.13 g, 1.3 mmol) was oxidised with *m*-CPBA (2.48 g, 1.43 mmol) in CH_2Cl_2 (150 ml) containing sodium carbonate (5.5 g), and after chromatography gave *2α,3α-epoxy-3β-vinyl-5α-cholestane* (15) (1.54 g, 28%), m.p. 100—101 °C (petroleum–ethanol); $\nu_{max.}$ ($CHCl_3$) 1 640 and 1 600 cm^{-1}; δ 5.76 (1 H, dd, *J* 17.5 and 9.5 Hz), 5.36 (1 H, dd, *J* 17.5 and 2.5 Hz), 5.2 (1 H, dd, *J* 9.5 and 2.5 Hz), 3.04 (1 H, d, *J* 6 Hz), 0.75 (3 H, s), 0.66 (3 H, s), and 2.1—0.9 (38 H, m) (Found: C, 84.36; H, 11.94. $C_{29}H_{48}O$ requires C, 84.44; H, 11.72%).

2-Methylenecyclohexanespiro-2′-oxiran (16).—1,2-Dimethylenecyclohexane (25) (17.6 g, 0.16 mol) on oxidation with peracetic acid (32 g, 38%, 0.16 mol) in CH_2Cl_2 (300 ml) containing sodium carbonate (42 g) gave the vinyloxiran (16) (11.2 g, 55%), b.p. 75 °C at 47 mmHg; δ 4.88 (1 H, s), 4.73 (1 H, s), 2.67 (2 H, s), and 2.48—0.7 (8 H, m).

(Oxiran-2-yl)cyclopent-1-ene (17).—Sodium hydride (4.4 g, 50%, 92 mmol) was combined with dry dimethyl sulphoxide (60 ml) and heated at 70—75 °C under nitrogen until effervescence ceased. The solution was diluted with dry THF (60 ml) and cooled to −2 °C. To this stirred solution was added, over a period of 3 min, trimethylsulphonium iodide (18.7 g, 92 mmol) in dry dimethyl sulphoxide (70 ml). The solution was then stirred for 1 min, and 1-formylcyclopent-1-ene (29) (8 g, 83 mmol) in dry THF (10 ml) added, such that the internal temperature of the reaction vessel did not rise above −2 °C. The reaction was allowed to attain room temperature, water (100 ml) was added, and the solution extracted with diethyl ether (3 × 200 ml). The ethereal extracts were dried (K_2CO_3), the solvent removed under reduced pressure, and distillation of the residue at reduced pressure yielded the *vinyloxiran* (17), (7.58 g, 83%), b.p. 80 °C at 20 mmHg; δ 5.85 (1 H, t, *J* 1.5 Hz), 3.52 (1 H, t), 2.83 (2 H, m), and 2.80—1.70 (6 H, m) (Found: M^+, 110.072 3. $C_7H_{10}O$ requires *M*, 110.073 2).

(2,3-Epoxypropylidene)cyclohexane (20).—Sodium hydride (1.47 g, 50%, 31 mmol) was combined with dry dimethyl sulphoxide (30 ml) and heated at 70—75 °C under nitrogen, until effervescence ceased. The solution was diluted with dry THF (30 ml), and cooled to −2 °C. To this stirred solution was added, over a period of 3 min, trimethylsulphonium iodide (6.32 g, 31 mmol) in dry dimethyl sulphoxide (25 ml). The solution was then stirred for 1 min, and the enal (30) (3.45 g, 28 mmol) in dry THF (5 ml) added, such that the internal temperature of the reaction vessel did not rise above −2 °C. The reaction was allowed to attain room temperature, water (50 ml) was added, and the solution extracted with diethyl ether (3 × 100 ml). The ethereal extracts were dried (K_2CO_3), the solvent removed at reduced pressure, and distillation of the residue at reduced pressure afforded the *vinyloxiran* (20) (3.17 g, 83%), b.p. 65 °C at 2 mmHg; δ 4.77 (1 H, d, *J* 8 Hz), 3.32 (1 H, AM_2X, *J* 8, 4, and 3 Hz), 2.77 (1 H, dd, *J* 5 and 3 Hz), 2.42 (1 H, dd, *J* 5 and 4 Hz), and 2.40—1.33 (10 H, m) (Found: M^+, 138.105 2. $C_9H_{14}O$ requires *M*, 138.104 5).

3,4-Epoxynon-1-ene (18).—Nona-1,3-diene (26) (3.66 g, 2.95 mmol) with *m*-CPBA (6.0 g, 2.99 mmol, 85%) in CH_2Cl_2 (50 ml) containing sodium carbonate (5 g) gave the *vinyloxiran* (18) (2.8 g, 68%), b.p. 66 °C at 13 mmHg; δ 5.74—4.96 (3 H, m), 3.12—0.66 (13 H, m) (Found: M^+ 140.1203 $C_9H_{16}O$ requires *M* 140.120 1).

3′-Vinylcyclohexanespiro-2′-oxiran (19).—Prop-2-en-ylidenecyclohexane (27) (20 g, 164 mmol), on oxidation with peracetic acid (32.8 g, 38%, 164 mmol) in CH_2Cl_2 (200 ml) containing sodium carbonate (43 g), afforded the *vinyloxiran* (19) (13.8 g, 61%), b.p. 72 °C at 18 mmHg; δ 6.1—5.3 (3 H, m), 3.12 (1 H, d *J* 5 Hz) and 1.97—0.7 (10 H, m) (Found: C, 78.27; H, 10.18. $C_9H_{14}O$ requires C, 78.21; H, 10.21%).

3,4-Epoxycyclohex-1-ene (21).—Cyclohexa-1,3-diene (28) (15 g, 0.18 mol) on oxidation with peracetic acid (38.8 g, 0.19 mol, 38%) in CH_2Cl_2 (200 ml) containing sodium carbonate (50 g) afforded the vinyloxiran (21) (10.3 g, 59%), b.p. 77—78 °C at 93 mmHg; $\nu_{max.}$ 2 900 and 1 640 cm^{-1}; δ 4.93 (2 H, d, *J* 4 Hz), 3.53—3.42 (1 H, m), 3.28—3.11 (1 H, m), and 2.41—1.43 (4 H, m).

General Procedure for Tricarbonyliron–Lactone Complex Preparation. Method A.—A solution of the vinyloxiran and pentacarbonyliron in de-gassed benzene was irradiated at room temperature under an argon atmosphere with two external 450-W Hanovia medium-pressure mercury lamps through Chance OX 1 filters. The reaction was followed by i.r. until the formation of the complex was maximised (2—6 h). Removal of the benzene and excess of penta-

carbonyliron under vacuum, taking care not to heat the mixture above 10 °C, gave the crude product. The product was stirred with ether and filtered through a pad of Celite. Trituration with petroleum afforded the crystalline complex.

Method B.—A solution of the vinyloxiran and pentacarbonyliron in de-gassed benzene was irradiated (10—15 min) using a 450-W Applied Photophysics lamp in an internal-well system and a circulating sodium bromide filter solution.[8] The product was worked up as above.

Preparation of Complex (1).—Using Method A (13) (0.54 g, 5.7 mmol) and $Fe(CO)_5$ (8.0 g, 40.8 mmol) in benzene (500 ml) gave the *tricarbonyliron complex* (1) (0.96 g, 65%) m.p. 104 °C; $\nu_{max.}$ 3 000, 2 130, 2 050, 1 680, 1 480, 1 400, 1 080, and 1 010 cm^{-1}; δ 3.97 (2 H, d, *J* 2 Hz), 3.44 (1 H, d, *J* 2 Hz), 2.64 (1 H, d, *J* 2 Hz), 2.14 (3 H, s) and 2.0 (3 H, s) (Found: C, 45.06; H, 3.62. $C_{10}H_{10}FeO_5$ requires C, 45.11; H, 3.76%).

Preparation of Complexes (2) *and* (3).—Using method A (14) (2 g, 18.2 mmol) and $Fe(CO)_5$ (15 g, 76.5 mmol) in benzene (500 ml) gave after chromatography on Florisil: (a) *the tricarbonyl-iron complex* (3) (0.54 g, 11%), m.p. 88—89 °C (decomp.); $\nu_{max.}$ 2 925, 2 075, 2 000, 1 680, 1 455, 1 390, 1 135, 1 115, 1 072, 995, 940, and 670 cm^{-1}; δ 4.61 (1 H, dd, *J* 12 and 9 Hz), 4.44—4.22 (1 H, br m), 3.5 (1 H, dd, *J* 9 and 2 Hz), 2.99 (1 H, dd, *J* 12 and 3 Hz), 2.76—2.44 (1 H, br m), 2.42—1.96 (4 H, m), and 1.64—1.2 (1 H, br, m) (Found: C, 47.35; H, 3.55; $C_{11}H_{10}O_5Fe$ requires C, 47.51; H, 3.62%): and (b) the *tricarbonyliron complex* (2) (3.24 g, 64%), m.p. 96—97 °C (decomp.); $\nu_{max.}$ 2 925, 2 075, 2 000, 1 990, 1 655, 1 465, 1 455, 1 375, 1 095, 1 085, 1 010, 990, 945, and 670 cm^{-1}; δ 5.34 (1 H, dd, *J* 8 and 12 Hz), 4.26 (1 H, t, *J* 6 Hz), 3.49 (1 H, dd, *J* 8 and 2 Hz), 2.78—2.42 (3 H, m), and 2.38—1.52 (4 H, m) (Found: C, 47.52; H, 3.81. $C_{11}H_{10}FeO_5$ requires C, 47.51; H, 3.62%).

Preparation of Complexes (4) *and* (5).—Using Method A (15) (1.24 g, 3 mmol) and $Fe(CO)_5$ (3.51 g, 18 mmol) in benzene (250 ml) gave after column chromatography on silica gel: (a) the *tricarbonyliron complex* (5) (0.5 g, 29%), m.p. 95 °C (decomp.); $\nu_{max.}$ ($CHCl_3$) 2 080, 2 000, and 1 665 cm^{-1}; δ 4.57 (1 H, dd, *J* 13 and 10 Hz), 4.39 (1 H, dd, *J* 12 and 3.5 Hz), 3.57 (1 H, dd, *J* 10 and 2 Hz), 3.05 (1 H, dd, *J* 13 and 2 Hz), 0.83 (3 H, s), 0.66 (3 H, s), and 2.2—0.9 (38 H, m) (Found: C, 68.01; H, 8.37. $C_{33}H_{48}FeO_5$ requires C, 68.2; H, 8.33%): and (b) the *tricarbonyliron complex* (4) (0.47 g, 27%), m.p. 90 °C (decomp.) (from ether); $\nu_{max.}$ ($CDCl_3$) 2 080, 2 000, and 1 660 cm^{-1}; δ 4.76 (1 H, dd, *J* 12 and 9 Hz), 4.4 (1 H, dd, *J* 12 and 5 Hz), 3.68 (1 H, dd, *J* 9 and 2 Hz), 3.0 (1 H, dd, *J* 12 and 2 Hz), 0.94 (3 H, s), 0.76 (3 H, s) and 2.3—0.9 (38 H, m) (Found: C, 68.18; H, 8.39. $C_{33}H_{48}FeO_5$ requires C, 68.27; H, 8.33%).

Preparation of Complex (6).—Using Method B compound (17) (1.53 g, 13.9 mmol) and $Fe(CO)_5$ (15.3 g, 78.1 mmol) in benzene (1 l) gave the *tricarbonyliron complex* (6) (2.77 g, 72%), m.p. 88.5—89.5 °C (decomp.); $\nu_{max.}$ 2 970, 2 100, 1 990, and 1 670 cm^{-1}; δ 4.73 (1 H, d, *J* 4 Hz), 4.48—3.94 (3 H, m), and 3.24—1.12 (6 H, m) (Found: C, 47.52; H, 3.65. $C_{11}H_{10}FeO_5$ requires C, 47.48; H, 3.6%).

Preparation of Complex (7).—Using Method A (16) (0.8 g, 6.45 mmol) with $Fe(CO)_5$ (8 g, 40.8 mmol) in benzene (400 ml) gave the *tricarbonyliron* complex (7) (560 mg, 29%), m.p. 83—84 °C (decomp.); $\nu_{max.}$ 2 900, 2 050, 1 990, 1 650, 1 465, 1 450, 1 380, 1 045, 995, 950, and 660 cm^{-1}; δ 4.13 (1 H, AB q, *J* 11.5 Hz), 3.77 (1 H, AB q, *J* 11.5 Hz), 3.15 (1 H, d, *J* 3 Hz), 2.53 (1 H, d, *J* 3 Hz), and 2.5—1.33 (8 H, m) (Found: C, 49.31; H, 4.03. $C_{12}H_{12}FeO_5$ requires C, 49.34; H, 4.14%).

Preparation of Complexes (8) *and* (9).—Using Method A compound (18) (0.8 g, 5.7 mmol) and $Fe(CO)_5$ (8 g, 40.8 mmol) in benzene (500 ml) gave 1.37 g (77%) of crude product which after chromatography on Florisil gave: (a) the *tricarbonyliron complex* (9) (240 mg, 18%) m.p. 97 °C (decomp.); $\nu_{max.}$ 2 900, 2 050, 1 992, 1 665, and 1 455 cm^{-1}; δ 4.96—4.6 (2 H, m), 4.3 (1 H, d, *J* 5 Hz), 3.7 (1 H, d, *J* 8 Hz), 3.12 (1 H, d, *J* 12 Hz), 1.7—1.1 (8 H, m), and 0.88 (3 H, br s) (Found: C, 50.96; H, 5.22. $C_{13}H_{16}FeO_5$ requires C, 50.67; H, 5.23%): and (b) the *tricarbonyliron complex* (8) (575 mg, 42%), m.p. 76—77 °C; $\nu_{max.}$ 2 850, 2 080, 2010, 1 660, 1 460, 1 070, 1 040, 995, and 660 cm^{-1}; δ 5.0—4.6 (2H, m), 4.05 (1 H, t, *J* 6.5 Hz), 3.78 (1 H, d, *J* 8 Hz, 3.08 (1 Hz), d, *J* 13 Hz), 1.9—1.14 (8 H, m), and 0.92 (3 H, br s) (Found: C, 50.45; H, 5.25. $C_{13}H_{16}FeO_5$ requires C, 50.67; H, 5.23%).

Preparation of Complex (10).—Using Method A compound (19) (0.8 g, 5.8 mmol) and $Fe(CO)_5$ (8 g, 40.8 mmol) in benzene (500 ml) gave the *tricarbonyliron complex* (10) (0.86 g, 49%), m.p. 96 °C (decomp.); $\nu_{max.}$ 2 925, 2 870, 2 050, 1 990, 1 670, 1 450, 1 440, 1 165, 985, 960, and 875 cm^{-1}; δ 5.14—4.58 (1 H, AM_2X, *J* 8, 9, and 13 Hz), 3.90 (1 H, d, *J* 8 Hz), 3.51 (1 H, d, *J* 9 Hz), 3.0 (1 H, d, *J* 13 Hz), and 2.13—1.18 (10 H, m) (Found: C, 50.82; H, 4.6. $C_{13}H_{14}FeO_5$ requires C, 51.01; H, 4.61%).

Preparation of Complex (11).—Using Method B compound (20) (1.23 g, 8.9 mmol) and $Fe(CO)_5$ (15.3 g, 78.1 mmol) in benzene (1 l) gave the *tricarbonyliron* complex (11) (1.27 g, 46%), m.p. 51—53 °C (decomp.); $\nu_{max.}$ 2 938, 2 855, 2 075, 2 015, 1 660, and 1 100 cm^{-1}; δ 4.98 (1 H, m), 4.70—3.86 (3 H, m), and 2.76—1.24 (10 H, m) (Found: C, 50.88; H, 4.60. $C_{13}H_{14}FeO_5$ requires C, 51.01; H, 4.61%).

Preparation of Complex (12).—Using Method A compound (21) (1 g, 10.4 mmol) and $Fe(CO)_5$ (10 g, 51.0 mmol) in benzene (400 ml) gave the *tricarbonyliron* complex (12) (0.86 g, 32%), m.p. 74 °C (decomp.) (lit.,[3c] 80 °C); $\nu_{max.}$ 2 900, 2 100, 1 990, 1 650, 1 460, 1 375, 1 340, 1 325, 1 060, 1 010, 995, 970, and 665 cm^{-1}; δ 5.84—5.68 (1 H, m), 5.44 (1 H, t, *J* 6 Hz), 4.7 (1 H, t, *J* 6 Hz), 4.57—4.44 (1 H, m), 2.64—1.92 (2 H, m), 1.78—1.5 (1 H, m), and 1.46—1.08 (1 H, m) (Found: C, 45.37; H, 3.16. Calc. for $C_{10}H_8FeO_5$: C, 45.58; H, 3.03%).

General Procedure for Oxidation with Cerium(IV) *Ammonium Nitrate.*—The complex was added in one portion to a stirred slurry of cerium(IV) ammonium nitrate at low temperature in the appropriate solvent. After complete oxidation (2—6 h) (as indicated by t.l.c.), the solvent was removed under reduced pressure. The residue was dissolved in the minimum amount of water and extracted with ether. The combined extracts were dried, and the solvent removed under reduced pressure to afford the lactones which were purified by chromatography.

Oxidation of Complex (1).—Compound (1) (50 mg, 0.19 mmol) with cerium(IV) ammonium nitrate (0.5 g, 0.9 mmol) in aqueous ethanol (14 ml; 50 : 50) at room temperature gave 3,6-dihydro-4,5-dimethyl-2-pyrone (34) (9 mg, 38%); $\nu_{max.}$ 2 875, 1 740, 1 620, 1 460, 1 440, 1 400, 1 380, 1 260, 1 210, 1 110, and 1 060 cm^{-1}; δ 4.72 (1 H, s), 2.96 (1 H, s), and 1.7 (6 H, s), identical by ^1H n.m.r. and i.r. to an authentic sample.[10]

Alternative Oxidation of Complex (1).—Compound (1) (0.5 g, 1.88 mmol) with cerium(IV) ammonium nitrate (6.18 g, 11.3 mmol) in acetonitrile (50 ml) at room temper-

ature gave, after chromatography on Florisil, 3-(*isopropenyl*)-3-*methyloxetan*-2-*one* (35) (98 mg, 42%) as an oil; $\nu_{max.}$ 2 940, 2 900, 1 825, 1 640, 1 450, 1 375, 1 150, 1 085, 930, 890, and 880 cm^{-1}; δ 4.96 (2 H, br, s), 4.28 (1 H, AB q, *J* 6.5 Hz), 4.05 (1 H, AB q, *J* 6.6 Hz), 4.05 (1 H, AB q, *J* 6.5 Hz), 1.83 (3 H, s), and 1.6 (3 H, s) [Found: $(M + 1)^+$ 127.076 1. $C_7H_{10}O_2$ requires $(M + 1)^+$ 127.075 9]: and 3,6-dihydro-4,5-dimethyl-2-pyrone (34) (38.4 mg, 16%) identical to the previous sample.

Oxidation of Complex (2).—The *syn*-complex (2) (910 mg, 3.27 mmol) with cerium(IV) ammonium nitrate (10.67 g, 19.5 mmol) in acetonitrile (50 ml) at −5 °C gave, after chromatography on Florisil, (a) 1-*vinyl*-6-*oxabicyclo*[3.2.0]-*heptan*-7-*one* (36) (230 mg, 51%) as an oil; $\nu_{max.}$ 2 900, 1 820, 1 635, 1 120, 1 100, 1 020, 960, 910, 875, and 820 cm^{-1}; δ 6.23—5.48 (1 H, m), 5.56—5.15 (2 H, m), 4.7 (1 H, d, *J* 3 Hz), and 2.41—0.63 (6 H, m) (Found: M^+ 138.068 1. $C_8H_{10}O_2$ requires *M*, 138.068 1): and (b) 2-*oxabicyclo*-[4.3.0]*non*-5-*en*-3-*one* (37) (137 mg, 29%) as an oil; $\nu_{max.}$ 2 930, 1 745, 1 300, 1 220, 1 210, 1 130, 1 090, and 1 065 cm^{-1}; δ(C_6D_6) 5.04—4.86 (1 H, m), 4.32 (1 H, br s), 2.66—2.35 (2 H, m), and 2.2—0.73 (6 H, m) (Found: C, 69.35; H, 7.55. $C_8H_{10}O_2$ requires C, 69.55; H, 7.30%).

Oxidation of Complex (3).—The *anti*-complex (3) (20 mg, 0.072 mmol) with cerium(IV) ammonium nitrate (0.235 g, 0.43 mmol) in acetonitrile (3 ml) at −5 °C gave 2-oxabicyclo[4.3.0]non-5-en-3-one (37) (7.4 mg, 75%) identical by t.l.c., n.m.r., and i.r. to the previous sample.

Oxidation of Complex (4).—Complex (4) (108 mg, 0.18 mmol) with cerium(IV) ammonium nitrate (652 mg, 1.08 mmol) in acetonitrile (6 ml) and benzene (6 ml) at room temperature gave after chromatography on Florisil: (a) 3β-*vinyl*-5α-*cholestano*[2,3-b]*oxetan*-2′-*one* (39) (10 mg, 12%), m.p. 139—140 °C (from petroleum); $\nu_{max.}$ 1 830 and 1 640; δ 5.98 (1 H, dd, *J* 17 and 10 Hz), 5.31 (1 H, d, *J* 17 Hz), 5.26 (1 H, d, *J* 10 Hz), 4.65 (1 H, dd, *J* 8 and 1.5 Hz), 0.72 (3 H, s), 0.66 (3 H, s) and 2.6—0.85 (38 H, m) (Found: C, 81.88; H, 11.18. $C_{30}H_{48}O_2$ requires C, 81.76; H, 10.98%): and (b) 2,3′-*dihydro*-5α-*cholestano*[2,3-b]*pyran*-2′-*one* (40) (23 mg, 27%), m.p. 145—146 °C (from methanol); $\nu_{max.}$ 1 730 and 1 640 cm^{-1}; δ 5.3 (1 H, br s), 5.05 (1 H, br m), 3.03 (2 H, br s), 0.82 (3 H, s), 0.64 (3 H, s), and 2.5—0.9 (38 H, m) (Found: M^+, 440.365 9. $C_{30}H_{48}O_2$ requires *M*, 440.365 4).

Oxidation of Complex (5).—Complex (5) (108 mg, 0.18 mmol) with cerium(IV) ammonium nitrate (656 mg, 1.08 mmol) in acetonitrile (6 ml) and benzene (6 ml) gave the δ-lactone (40) (20.3 mg, 25%) identical by t.l.c., m.p., and ^1H n.m.r. to the previous sample.

Oxidation of Complex (6).—Complex (6) (500 mg, 1.8 mmol) with cerium(IV) ammonium nitrate (4.93 g, 9 mmol) in absolute ethanol at −15 °C, gave after chromatography at 0 °C on silica gel, 3-(cyclopent-1-en-1-yl)oxetanone (38) (198 mg, 100%); $\nu_{max.}$ 2 950, 2 860, 1 825, 1 635, and 1 115 cm^{-1}; δ 5.7 (1 H, br s) 4.60—4.14 (3 H, ABC system), 2.36 (4 H, m), and 1.92 (2 H, m) (Found: M^+, 138.067 7. $C_8H_{10}O_2$ requires *M*, 138.068 1).

Oxidation of Complex (7).—Complex (7) (207 mg, 0.71 mmol) with cerium(IV) ammonium nitrate (20.6 g, 37.6 mmol) in acetonitrile (15 ml) at −5 °C after chromatography on Florisil gave: (a) 2-methylenecyclohexane-spiro-4′-oxetan-2′-one (41) (16.1 mg, 15%) as an oil, $\nu_{max.}$ 2 925, 2 850, 1 830, 1 640, 1 450, 1 285, 1 140, 1 110, 1 095, 1 080, 1 060, 980, 920, and 900 cm^{-1}; δ(C_6D_6) 4.83 (1 H, s), 4.60 (1 H, s), 3.65 (1 H, AB q, *J* 5.5 Hz), 3.35 (1 H, AB q, *J* 5.5 Hz), and 2.33—0.67 (8 H, m) [Found: $(M + 1)^+$ 153.091 8. $C_9H_{12}O_2$ requires $(M + 1)$, 153.091 6]: and (b) 5,6,7,8-tetrahydroisochroman-3-one (42) (59.2 mg, 55%) as an oil; $\nu_{max.}$ 2 900, 1 740, 1 635, 1 225, and 1 045 cm^{-1}; δ 4.63 (2 H, br s), 2.88 (2 H, br s), and 2.05—1.45 (8 H, m).

Oxidation of Complex (8).—Complex (8) (120 mg, 0.39 mmol) with cerium(IV) ammonium nitrate (1.28 g, 2.33 mmol) in acetonitrile (15 ml) at −30 °C gave trans-4-*pentyl*-3-*vinyloxetan*-2-*one* (44) (44.3 mg, 68%) as an oil; $\nu_{max.}$ 2 925, 2 850, 1 830, 1 640, 1 460, 1 380, 1 130, 990, 935, and 875 cm^{-1}; δ 6.13—5.78 (1 H, m), 5.46—4.24 (2 H, m), 4.47—4.31 (1 H, m), 3.88 (1 H, dd, *J* 4 and 8 Hz), 1.98—1.1 (8 H, m), and 0.9 (3 H, t, *J* 7 Hz) (Found: C, 71.65; H, 9.35. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%).

Oxidation of Complex (9).—Complex (9) (240 mg, 0.78 mmol) with cerium(IV) ammonium nitrate (2.56 g, 4.67 mmol) in acetonitrile (25 ml) at −30 °C gave cis-4-*pentyl*-3-*vinyloxetan*-2-*one* (45) (84 mg, 64%) as an oil; $\nu_{max.}$ 2 925, 2 850, 1 830, 1 640, 1 460, 1 275, 1 130, 1 110, 990, 940, and 875 cm^{-1}; δ 6.04—5.66 (1 H, m), 5.54—5.3 (2 H, m), 4.54 (1 H, t, *J* 7 Hz), 4.36 (1 H, t, *J* 7 Hz), 1.9—1.1 (8 H, m), and 0.9 (3 H, t, *J* 7 Hz) (Found: C, 71.15; H, 9.8. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%).

Oxidation of Complex (10).—Complex (10) (430 mg, 1.4 mmol) with cerium(IV) ammonium nitrate (4.58 g, 8.35 mmol) in acetonitrile (35 ml) at −5 °C gave 3′-vinylcyclohexanespiro-4′-oxetan-2′-one (46) (121 mg, 52%) as an oil; $\nu_{max.}$ 2 940, 2 850, 1 830, 1 640, 1 450, 1 280, 1 195, 1 020, 885, 820, and 810 cm^{-1}; δ 5.68—4.68 (3 H, m), 3.26 (1 H, d, *J* 6 Hz) and 1.7—0.64 (10 H, m).

Oxidation of Complex (11).—Complex (11) (300 mg, 0.98 mmol) with cerium(IV) ammonium nitrate (2.16 g, 3.94 mmol) in methanol at −78 °C gave, after column chromatography on silica gel at 0 °C, an oil ($\nu_{max.}$ 2 940, 1 820, cm^{-1}) which was immediately reduced to the diol (54) with lithium aluminium hydride in diethyl ether (see later).

Oxidation of Complex (12).—Complex (12) (290 mg, 1.09 mmol) with cerium(IV) ammonium nitrate (3.61 g, 6.6 mmol) in ethanol (15 ml) at −5 °C gave 7-oxabicyclo-[4.2.0]oct-2-en-8-one (47) (116.8 mg, 86%) as an oil; $\nu_{max.}$ 2 900, 1 815, 1 440, 1 420, 1 360, 1 310, 1 280, 1 225, 1 125, 1 065, 1 025, 970, 880, 850, 795, 745, 690, and 675 cm^{-1}; δ 6.3—6.0 (1 H, m), 5.85—5.53 (1 H, m), 4.91—4.73 (1 H, m), 4.1 (1 H, t, *J* 6 Hz), and 2.45—0.98 (4 H, m).

General Procedure for the Reduction of the Lactones with Lithium Aluminium Hydride.—A solution of the lactone in dry tetrahydrofuran (THF) was added dropwise to a stirred slurry of lithium aluminium hydride in tetrahydrofuran. After t.l.c. indicated complete reaction, saturated sodium sulphate was cautiously added to the mixture to produce a white precipitate. The mixture was filtered and the precipitate washed with copious amounts of ether. The combined organic phases were dried and after removal of the solvent gave the diol.

Reduction of (35).—Compound (35) (130 mg, 1.03 mmol) with lithium aluminium hydride (120 mg, 3.15 mmol) in THF (10 ml) gave 2-(*isopropenyl*)-2-*methylpropane*-1,3-*diol* (48) (117 mg, 87%), m.p. 56.5—57.5 °C; $\nu_{max.}$ 3 350, 2 950, 1 640, 1460, 1 030, and 895 cm^{-1}; δ 5.0—4.93 (1 H, m), 4.85 (1 H, s), 3.75 (4 H, d, *J* 2 Hz), 2.84 (2 H, s), 1.79 (3 H, br s), and 1.0 (3 H, s) (Found: C, 64.75; H, 10.8. $C_7H_{14}O_2$ requires C, 64.58; H, 10.84%).

Reduction of (36).—Compound (36) (150 mg, 1.1 mmol) with lithium aluminium hydride (200 mg, 5.2 mmol) in

THF (10 ml) gave 2-(*hydroxymethyl*)-2-*vinylcyclopentanol* (49) (108 mg, 70%); $\nu_{max.}$ 3 325, 2 925, 1 640, 1 410, 1 050, 1 040, 1 010, and 910 cm^{-1}; δ 5.86 (1 H, q, *J* 10 and 18 Hz), 5.25—4.96 (2 H, m), 4.25—4.11 (1 H, m), 3.69 (2 H, s), 3.05—2.25 (2 H, m), and 2.15—1.18 (6 H, m) (Found: C, 67.4; H, 10.15. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%).

Reduction of (37).—Compound (37) (138 mg, 1 mmol) with lithium aluminium hydride (200 mg, 5.2 mmol) in THF (10 ml) gave 2-(syn-3′-*hydroxyprop*-1-*enyl*)*cyclopentanol* (50) (100 mg, 70.4%), m.p. 52.5—53 °C; $\nu_{max.}$ 3 350, 3 280, 2 950, 2 920, 1 440, 1 065, 1 030, 970, 945, 920, 900, 875, and 865 cm^{-1}; δ 5.4 (1 H, t, *J* 8 Hz), 4.5 (1 H, s), 4.06 (2 H, s), 3.87—3.16 (2 H, m), and 2.74—0.8 (8 H, m) (Found: C, 67.6; H, 10.2. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%).

Reduction of (38).—Compound (38) (100 mg, 0.73 mmol) with lithium aluminium hydride (100 mg, 2.6 mmol) in diethylether (10 ml) gave 2-(*cyclopent*-1-*en*-1-*yl*)*propane*-1,3-*diol* (51) (36.2 mg, 35%), m.p. 45—46 °C; δ 5.46 (1 H, bds), 3.86 (2 H, d, *J* 5 Hz), 3.76 (2 H, d, *J* 5 Hz), 2.66 (1 H, t, *J* 5 Hz), and 2.48—1.62 (8 H, m) (Found: C, 67.4; H, 9.9. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%).

Reduction of (41).—Compound (41) (16.1 mg, 0.1 mmol) with lithium aluminium hydride (100 mg, 2.6 mmol) in THF (20 ml) gave 1,1-*bis*(*hydroxymethyl*)-2-*methylenecyclohexane* (52) (7.7 mg, 47%), m.p. 68.5 °C (from petroleum); $\nu_{max.}$ 3 320, 3 080, 2 930, 2 855, 1 635, 1 475, 1 440, 1 372, 1 100, 1 047, 1 035, 1 020, 1 000, and 892 cm^{-1}; δ 4.9 (1 H, s), 4.75 (1 H, s), 3.7 (4 H, d, *J* 4 Hz), 2.5—2.0 (2 H, m), and 1.54 (6 H, br s) (Found: C, 69.15; H, 10.35. $C_9H_{16}O_2$ requires C, 69.19; H, 10.32%).

Reduction of (42).—Compound (42) (54.9 mg, 0.36 mmol) with lithium aluminium hydride (150 mg, 3.9 mmol) in THF (6 ml) gave 2-[1-(*hydroxymethyl*)*cyclohex*-1-*enyl*)-*ethanol* (53) (44.6 mg, 79%) as an oil; $\nu_{max.}$ 3 340, 2 930, 2 880, 2 830, 1 665, 1 435, 1 045, 1 015, and 1 000 cm^{-1}; δ 4.05 (2 H, s), 3.66 (2 H, t, *J* 6 Hz), 3.9—3.7 (2 H, m, exchangeable with D_2O), and 2.5—1.35 (10 H, m) (Found: C, 69.1; H, 10.25. $C_9H_{16}O_6$ requires C, 69.19; H, 10.32%).

Reduction of (43).—Compound (43) [crude product from oxidation of complex (11)] with lithium aluminium hydride (200 mg) in diethyl ether (25 ml) gave 2-(*cyclohexylidene*)-*propane*-1,3-*diol* (54) (72.1 mg, 43.2%) as an oil; δ 4.9 (1 H, m), 4.07 (1 H, m), 3.7—3.0 (5 H, m), and 2.37—1.1 (11 H, m) (Found: C, 70.4; H, 10.75. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.66%).

Reduction of (46).—Compound (46) (121 mg, 0.73 mmol) with lithium aluminium hydride (200 mg, 5.2 mmol) in THF (10 ml) gave 2-(1-*hydroxycyclohexyl*)*but*-3-*en*-1-*ol* (55) (90 mg, 72%) as an oil; $\nu_{max.}$ 3 370, 2 940, 2 860, 1 640, 1 450, 1 420, 1 160, 1 080, 1 050, 1 015, 1 000, 970, and 920 cm^{-1}; δ 6.18—5.5 (1 H, m), 5.3—4.9 (2 H, m), 3.8 (2 H, d, *J* 6 Hz), 2.83—2.11 (3 H, m), and 1.73—1.26 (10 H, m) (Found: C, 70.4; H, 10.9. $C_{10}H_{18}O_2$ requires C, 70.54; H, 10.65%).

Reduction of (47).—Compound (47) (89 mg, 0.71 mmol) with lithium aluminium hydride (100 mg, 2.6 mmol) in THF (10 ml) gave the diol (56) which was immediately converted into 2-(*hydroxymethyl*)*cyclohex*-3-*en*-1-*ol bis*(*toluene*-p-*sulphonate*); δ 7.74 (4 H, d, *J* 8 Hz), 7.3 (4 H, d, *J* 8 Hz), 5.9—5.55 (1 H, m), 5.43—5.13 (1 H, m), 5.0—4.7 (1 H, m), 3.9 (2 H, d, *J* 7 Hz), 2.41 (6 H, s), and 2.22—1.0 (4 H, m) (Found: C, 57.7; H, 5.45; S, 15.05. $C_{21}H_{24}O_6S_2$ requires C, 57.79; H, 5.5; S, 14.67%).

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